General aspects of carbon biogeochemistry in the ria of Vigo, northwestern Spain

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Abstract-The rias of Galicia in northwestern Spain are local areas of high primary production. In this article, the fluxes of organic and inorganic carbon and the processes of photosynthesis, remineralization, and sedimentation of particulate organic carbon in one of these, the ria of Vigo, are quantified using the box model method. In 1986 the mean photosynthesis rate in the ria of Vigo was 350 mgC m^{-2} d^{-1}; on average, 40% of this quantity was remineralized; 140 mgC m^{-2} d^{-1} passed into the sediment; and the remaining 65 mgC m^{-2} d^{-1} (18%) was exported to the coastal waters. Such budgets are very sensitive to meteorologic conditions; for during the April to October period when wind-induced upwelling is frequent, the processes mentioned increase greatly in the interior part of the ria. In winter a large quantity of carbon gets exported to the ocean, 78 molC s^{-1}. During the rest of the year the ria behaves like a carbon trap, with most of the 27 molC s^{-1} that is trapped being lost to sedimentation.

INTRODUCHON

THE PHOTOSYNTHESIOS F organic matter in the rias of Galicia is enhanced by the input of nutrient salts (PREGO, 1990a) resulting from the Finisterre marine upwelling (FRAGA, 1981). This upwelling, which occurs from April to October (BLANTON et al., 1984), brings North Atlantic Central Water (NACW) to the interior of the rias (PREGO and FRAGA, 1992). According to the data obtained before 1986, the primary production in the middle zone of the rias generally ranges between 30 to 100 mgC m^{-2} d^{-1} (VIVES and FRAGA, 1961; GONZALEZ et al., 1982) in the winter, but this increases to 700 to 1200 mgC m^{-2} d^{-1} during the rest of the year (VIVES and FRAGA, 1961; NUNES et al., 1984). Thus, the annual mean production of this part of the rias fluctuates around 710 mgC m^{-2} d^{-1} (FRAGA, 1976; VARELA et al., 1984). These values are somewhat lower than those given by WOLFF (1980) for some estuaries. This is due to the fact that, although the Galician rias have been considered as estuaries from a geological point of view (FAIRBRIDGE, 1980), hydrologically, they are only considered as such in their inner part. In box 1 (Fig. 1) the salinity is below 15 PSU (Practical Salinity Units) during high freshwater fluvial inputs (SAIZ et al., 1961; PREGO et al., 1988).

Because the rias are zones of relative high primary production, compared with nearby oceanic regions (FINENKO, 1978), they should exhibit elevated processes of remineralization and sedimentation of the organic matter in the sea (MENZEL, 1974).

The distribution of carbon in the ria of Vigo and its interchange with the surrounding eastern North Atlantic coastal waters will thus be affected by physical processes like residual estuarine circulation, mixing, and upwelling (PREGO et al., 1990), as well as by the suite of biogeochemical reactions which have been recognized to be accelerated in estuaries (OLAUSSON, 1980). On the Galician coast of Spain, particulate organic matter (POM) shows a marked seasonal variation with a winter minimum and two maxima, one in spring and the other at the end of the summer (FRAGA, 1960, 1981). However, the cycling of carbon has not been rigorously investigated in the rias of Galicia, other than to hypothesize that the variation of inorganic and organic carbon will be similar to that of the nutrient salts (MOURIRO et al., 1984) and organic matter, respectively (FRAGA, 1960), forced by the general relationships defined by REDFIELD (1934).

SAMPLING AND ANALYSES

Samples were taken at five stations along the principal axis of the ria (Fig. 1), together with another at its northern mouth and three to seaward, out to the 150 m isobath. As water depth permitted, sampling depths were 0, 5, 10, 20, 30, 40, 50, 60, 80, 100, 120, 150 m, and the seabed. This transect was repeated six times, from February until October 1986.

The position of the stations in the narrows of the ria divided it into five boxes (Fig. 1). Their dimensions are given in Table 1. The sampling and the analyses were carried out on board R/V Garcia de1 Cid. The samples of water were taken in Niskin bottles of 1.7 L capacity. From these, subsamples were taken for the analysis of dissolved oxygen, alkalinity, and organic carbon.

The analysis of dissolved oxygen was based on the Winkle method. The estimation was made with a Metrohm automatic titrator and a silver electrode. The estimated precision of this titration is ± 1 μmol kg^{-1}.

The determination of organic carbon was carried out according to the method described by PREGO and FRAGA (1988), in which organic matter is oxidized with potassium peroxidisulphate under UV light. The precision of this method is estimated as ± 2 μmol kg^{-1}.

The total alkalinity was determined by estimation in a Metrohm automatic titrator, according to the method described by PEREZ and FRAGA (1987a). The precision is ± 2 μmol kg^{-1}.

Total inorganic carbon was then calculated from the salinity, alkalinity, and pH data as described by PEREZ and FRAGA (1987b). The precision is estimated to be ± 1.5 μmol kg^{-1}.

METHODS AND RESULTS

The method used in this study of the biogeochemistry of carbon in the ria of Vigo is based on the fact that, in any volume of water considered, it is true for the parameters chosen that

$$dN/dt = \text{fluxes} + \text{biogeochemical processes} = 0. \qquad (1)$$

With regard to the fluxes and processes the criteria of signs are inputs to a box or a layer are positives and outputs are negatives.

Fluxes in a Two Box Model

The ria of Vigo, like the other rias of Galicia (OTTO, 1975; FRACA and MARGALEF, 1979; GONZALEZ et al., 1979; FERNANDEZ DE CASTILLEJO and LAWN, 1982; PREGO et al., 1990), shows a positive estuarine circulation (Figs. 5 and 6). There is a current which outflows at the surface, another which inflows along the bottom, and a region of partial mixing between the two. This has been conceptualized in model form by PREGO and FRAGA (1992).

Consider now a series of domains "boxes" (boxes dl- 1 to B-S in Figs. 1 and 2) which are created by the series of sections (Fig. 1) perpendicular to the axis of the ria (upper subsections: S-1 to S-9, and lower subsections: S-10 to S-90; Fig. 2). The inflows and outflows of the ria divide each box into two layers (L2 to L5 and L20 to L50 in Fig. 2) and twenty-five flux terms ("F" in Fig. 2). Due to the estuarine nature of box B-1, as previously mentioned, it has not been divided into two layers. In the other boxes, the flushing time is much longer than a tidal cycle, advection is due to net flow (PREGO and FRAGA, I992), and the tidal current only acts on the mixing process, as OTTO (1975) has indicated for the ria of Arosa.

Since the flux of a substance is equal to the product of the flow multiplied by its concentration, it is necessary to know both values. The residual estuarine flows (Table 2) have been reported by PREGO and FRAGA (1992). The mean concentrations (Table 3) were calculated from these data (PREGO et al., 1988), and then averaged with respect to area, in the case of the subsections of separation of the boxes, or averaged with respect to volume, in the general case of the two layer system.

The resulting fluxes for the ria are summarized in Table 4.

Balance in a Two Box Model

According to (I), two balances can be established for each box,

upper layer: $\Sigma\, Fi + A = 0$ (2)

lower layer: $\Sigma\, Fi + B = 0$, (3)

where positive Fi are inputs to a given layer and negative Fi are outputs from that layer.

The biogeochemical processes A and B will be zero if there are only physical processes of inflow, outflow, or exchange between the two layers. By corollary, they will be different from zero if there is a loss, gain, or transformation of substances in a box or a layer (Fig. 3). Note that the A or B values will be negative if the flux inputs are greater than the flux outputs.

The results for a two layer system (*A* = upper layer, *B* = lower layer) are shown in Table 5. They were obtained using flux data (Table 4) and Eqns. 2 and 3.

Quantification of the Interchange of Carbon

The biogeochemical processes which take place in the ria of Vigo cause disequilibrium in the distribution of organic and inorganic carbon in the water. The production of particles by photosynthesis (P), sinking of POM (D), remineralization (R), and sedimentation (S) in the ria drive the overall balance away from zero. In other words, these processes result in a net exchange of carbon between layers, as shown in Fig. 3. To complete the mass balance it is also necessary to include the transfer of CO_2 gas between the water of the ria and the atmosphere (C) and the interchanges due to the formation and redissolution of carbonate (Cs and Cd).

Following the convention for signs explained in the preceding section, the mass balance of dissolved inorganic carbon in the upper layer, A1, will decrease due to photosynthesis (P), $CaC0_3$ formation (Cs) and the transfer of CO_2 to the atmosphere (C). The companion inorganic carbon mass balance B1 in the lower layer will increase due to remineralization (R) and the redissolution of $CaC0_3$ (Cd; Fig. 3). Similarly, the mass balance of particulate organic carbon (POC) in the upper layer (A2) will decrease due to the sinking (D) of POM. That for the lower layer (B2) will decrease by remineralisation (R) and by sedimentation of POM, and will increase by the arrival of POM from the surface (D; Fig. 3).

There are seven unknowns (C, P, D, R, S, Cs, and Cd) and only four equations corresponding to the balances A1, A2, B1, and 82. The other three needed to reach a solution come from the interchange of CO_2 and $CaCO_3$. For their estimation it is necessary to use the alkalinity and the “CAO” a biogeochemically conservative parameter for carbon (see Appendix).

The result of the balance of CA0 in the upper layer is A0 and increases with the passage of 0_2, Og, and $C0_2$, C, from the sea to the atmosphere, whilst the balance in the lower layer is BO and, being isolated from the atmosphere, its balance must be zero (Fig. 3).

The value of the balance of alkalinity (A3 and B3) increases in both layers when ions of strong acid or bases appear. Consequently, the consumption of ammonia and the precipitation of carbonate will decrease the value, while the consumption of nitrate and nitrite will increase it (Fig. 3).

Now condensing the derivations given,

-System I-

$$A0 = Og + 1.36C \qquad (4)$$

$$BO = 0 \qquad (5)$$

$$A1 = C + Cs + P \qquad (6)$$

$$B1 = Cd + R \qquad (7)$$

$$A2 = - P + D \qquad (8)$$

$$B2 = - R - D + S \qquad (9)$$

$$A3 = - (P3 + P2 - P4) + 2Cs \qquad (10)$$

$$B3 = - (R3 + R2 - R4) + 2Cd, \qquad (11)$$

where 1.36 is the conversion factor for moles of carbon to moles of oxygen, and 2 is a factor which reflects the fact that precipitation of a mole of $CaCO_3$ eliminates two equivalents of strong base. The values "Og" (oxygen), F3, F2, P4 (nitrate, nitrite, and ammonia consumed by photosynthesis), and R3, R2, R4 (nitrate, nitrite, and ammonia remineralized) are calculated (PREGO, 1988) by NO (see Appendix), nitrate, nitrite, and ammonia balances (Tables 8 and 9). These results, together with values taken from Table 5, are applied to system I and the summary results are given in Table 6. In these data, the error caused by a small spatial or temporal variation of concentration of POC should not be important, in accordance with the photosynthesis values, the concentration of chlorophyll, and the biomass of phytoplankton obtained in different areas in the ria during one annual cycle (VIVES and FRAGA, 196 1; FRAGA, 1960, 1976).

The main source of error is the estimation of freshwater flowing into the ria, since the flow rates depend on it (PREGO and FRAGA, 1992). Consequently the results given in Tables 2 and 4 can vary individually by 10% (PREGO et al., 1990). The errors in the chemical parameters analyzed, in turn, make the final error in each measurement ± 1 mol s^{-1} for the entire ria for the values of Tables 6 and 7, and ± O.5 mol s^{-1} for the ria as a whole for Tables 5, 8, and 9.

In the approach described, the value of BO (Table 5) should be zero because the lower layer is not in contact with the atmosphere. The small discrepancy may be caused, in addition to the sources of error described above, by a greater penetration of CO_2 and O_2 into the deeper water during winter storms or by differences in vertical distribution of phytoplankton in the summer. The latter can result in phytoplankton taking up nutrients in the bottom box, while photosynthesis occurs in the top box (FRAGA and PREGO, 1989).

DISCUSSION

Seasonal Variation of the Organic Carbon

Monthly average rainfall data for 1986 indicates that precipitation that year was similar to the mean of the last 30 years. Hence, since 1986 may be considered as a normal year and the water flows have been calculated in quasi-stationary conditions (PREGO and FRAGA, 1992), results should be representative of the different seasons in the ria of Vigo.

In most of the six sampling periods in 1986, photosynthesis generally remained between 20 and 40 mol s^{-1} for the entire ria (Table 6) that is, around 300 mgC m^{-2} d^{-1}. However, this production can change dramatically in the ria of Vigo between summer and winter, or during periods of strong upwelling. Consequently, three very different regimes for organic carbon cycling may be considered, as shown in Fig. 4.

The situation in February 1986 (Fig. 4a) may be taken as representative of the winter, based on the meteorological and hydrographic conditions (PREGO et al., 1990). Calculated photosynthesis (P) in the water column is net photosynthesis; i.e., it is the difference between photosynthesis and remineralisation in the upper layer. On the 28th of February net remineralization occurs in all seawater of the ria (6 mol s^{-1} in upper layer and 18 mol s^{-1} in lower layer). The sediment yields 26 mol s^{-1} to the water column, a flux which is similar to the annual mean sedimentation, but with the opposite sign.

This resuspension occurs in box 2 (Table 6), when inflow of estuarine water is substantial, caused by the strait and the sharp bathimetry (from 5 to 23 m of depth) between boxes 1 and 2 (see Fig. 1). Thus, inflow along the bottom, resuspension, and the inflow of freshwater at the surface are the principal wintertime contributors of organic carbon to the ria. Due to the vigorous circulation in this rainy period (PREGO and FRAGA, 1992), there is a high influx (118 molC s^{-1}) and outflux (138 molC s^{-1}) of organic carbon (Fig. 4a and Table 4). The organic matter influx must be only slightly labile (AMINOT et al., 1990); from Fig. 4a it is clear that most of it leaves the ria without being transformed.

After the spring bloom of phytoplankton the situation in the ria becomes stable (Fig. 5). On May 26th (Fig. 4b), as well as in July (Table 4), there is little net interchange of organic carbon between the ria and the continental shelf. Consequently, the POC all falls to the lower layer, where 74% (85% in July) of organic carbon photosynthesized (Fig. 4b and Table 6: 195 mgC m^{-2} d^{-1}) sediments out and the rest is remineralized.

Another modification to primary production occurs when there is marine upwelling in spring. On May 31st, after five days of strong northerly winds (PREGO and FRAGA**,** 1992), the production had doubled (430 mgC m^{-2} d^{-1}; Table 6).

Again on the 4th of September, upwelling was intense (PREGO et al., 1990) and the NACW had reached the bed of the ria (Fig. 6). The production was 105 molC s^{-1}, that is, 945 mgC m^{-2} d^{-1}. The net export of POC to the continental shelf was 36% of the production. In fact, outside the ria this POC sinks, and it can be seen in the nitrate isopleths (Fig. 6) as a seasonally (PREGO et al., 1988) intense remineralisation on the continental shelf, as PREGO (1990b) has shown. Moreover this sinking organic carbon shows up as an entry to the ria which is 19% of the POC produced (Fig. 4c). When the upwelling relaxes, however, sedimentation slows and remineralisation becomes the more important process. By September 21st eighty-six upwellings had ceased, and the circulation in the ria had almost stopped (FRAGA and PRECO 1989). Now sedimentation was negligible, and remineralisation tied up practically 100% of the POM which fell (PREGO, 1992), and an intense red tide appeared (FRAGA et al., 1990).

Annual Budgets

The mean annual value of photosynthesis for 1986, estimated from Table 6, is 350 mgC m^{-2} d^{-1} for all the ria and 790 mgC m^{-2} d^{-1} in boxes 2-3. This value is similar to that measured directly using 14C at an interior station of the ria of Vigo (VIVES and FRAGA, 1961; FRAGA, 1976). The mean annual remineralization (145 mgC m^{-2} d^{-1}) in the ria is approximately equal to 40% of the photosynthesis. Some 140 mgC m^{-2} d^{-1} is sedimented, i.e., 40% of net photosynthesis, similar to 33% of the average rate of organic carbon sedimentation in continental margin (ROMANKEVICH, 1984) during Late Quaternary or 32% sedimented in coastal zones estimated by WOLLAST (1991). The rest of the organic carbon, some 18% of the production (65 mgC m^{-2} d^{-1}), is available for export to adjacent coastal waters. This agrees with the WOLLAST (1991) tentative mass balance of the organic flux on the continental shelf and slope in which 15% of organic carbon production is exported from coastal zone.

Sedimentation of organic-rich matter is favoured, with respect to water column remineralization, by the shallowness of the ria. The thickness of sediment formed annually (50 gC m^{-2}), in accordance with its composition (approximately 3% of organic carbon; NOMBELA et al., 1987), is of the same order as that of 1 mm $year^{-1}$ estimated by MARGALEF (1956) near station 3 (Fig. 1). However, "sedimentation" must include any disappearance of POM in the water layer brought about by causes other than reminerahzation, including fishing (1.5 10^6 Kg) and mussel cultivation (8.0 10^7 Kg) in the ria (EQUIPO BIOLOGIA PESQUERA, 1987). This implies that man takes close to 20 mgC m^{-2} d^{-1}**,** of which 14 mgC m^{-2} d^{-1} is from mussels alone.

Property-property plots of sinking (D), remineralisation *(R),* and sedimentation (S) of POC vs. photosynthesis in the ria of Vigo are shown as Fig. 7. Based on the information in Table 6 and summing for boxes 2, 3, and 4, the following correlations are obtained:

$$D = -18 + 0.37P \qquad r = 0.89 \qquad (12)$$

$$R = -8.4 - 0.59P \qquad r = 0.98 \qquad (13)$$

$$S = -10 + 0.19P \qquad r = 0.86, \qquad (14)$$

where the sink in POC, its remineralization, and sedimentation can be estimated from the average photosynthesis value in the ria of Vigo. Equations 12, 13, and 14 were obtained in accordance with the sign criteria used in this article; i.e., photosynthesis is negative if organic carbon is consumed. Values *P, D, R,* and S are at molC s^{-1}, but these are easily converted to mgC m^{-2} d^{-1} by multiplying them by 10.6.

The robust correlations ‘Y’ between photosynthesis and sinking, remineralization, and sedimentation, as calculated from Eqns. 12, 13, and 14, presumably arise because the ria of Vigo is a shallow, semi-enclosed bay (156 km^2) which is hydrographically distant from the adjacent shelf (PREGO and FRAGA, 1992).

Zonal Distribution of the Organic Carbon

The processes just discussed for the ria of Vigo as a whole can also be dissected into zones by partitioning the ria into the five boxes shown in Figs. 1 and 2. Table 6 presents the results of such a compartmentalization.

The late spring state, corresponding to May 26th, is similar to that during the decline of the upwelling in July or October. At these times box 4 (14 molC s^{-1}; Table 6) is the most productive, although per unit area box 2 has the highest rates (620 mgC m^{-2} d^{-1}; Table 6). These two zones show the locally highest concentrations of chlorophyll (Fig. 5), and locally high concentrations of organic carbon are present in the sediment underlying these two zones (NOMBELA et al., 1987).

The sinking of POM permits the ria to be divided into two zones as well: (a) an interior zone (boxes l-3), where the photosynthesis is greater than the loss, and (b) the outer two zones, where the fall of POM is greater. Note that both remineralisation and sedimentation increase towards the month of the ria (Table 6).

The late summer state during upwelling shows an important change. On the 4th of September the concentration of chlorophyll was very high (Fig. 6) and the production was correspondingly high throughout the ria (950 mgC m^{-2} d^{-1}). In box 2 it is five times greater per unit area than in the rest of the ria, to account for almost half the total (Table 6: 700, 3710, 1010, and 480 mgC m^{-2} d^{-1} in boxes 1, 2, 3, and 4, respectively). In this time of enhanced production, the planktonic cycle restarts, as reported by MARGALEF et al. (1955). Because the utilization of silica is high, sediments produced in box 2 in late summer are rich in diatoms (MARGALEF, 1958). In fact, the locally high production of zone 2 of the ria had already been recognized by MARGALEF et al. (1955) as well as by VlVES and FRAGA (1961). FRAGA (l976) has pointed occasionally to a primary production of 2800 mgC m^{-2} d^{-1} by ^{14}C in this area of the ria. OTTO (1975) reported the existence of a similar zone of locally enhanced production (2000 mgC m^{-2} d^{-1}) in the ria of Arosa, which is also dependent on the upwelling of Finisterre (FRAGA, 1981).

Remineralization, however, consumed over 73% of the photosynthesis. POC sinks in boxes 3 and 4 and is transported in incoming current to the lower layer to box 2, where it is remineralized (2730 mgC m^{-2} d^{-1}). The accumulation of POM on the bed of the ria of box 3 was also high (650 mgC m^{-2} d^{-1}), almost six times higher than on the 26th of May.

Consequences: Exchange of Carbon between the Ria and Its Surroundings

Exchanges of carbon between the ria of Vigo and its boundaries are summarized in Table 7 and correspond to:

The transfer of CO_2 between the atmosphere and the water

The passage of CO_2 air-water has been considered as a correction to the balance of inorganic carbon (Eqn. 6) in the upper layer of the ria (PREGO, 1992). For this reason, and since the net flux of CO_2 is very close to the range of error, it would be advisable to deal with this matter in another paper.

Although the transfer of CO_2 was small relative to the fluxes of POC, there were two exceptions. One, during the late summer period of upwelling, when a cooling and mixing of the waters occurs (PREGO et al., 1990) and there is high primary production, (12 molC s^{-1}) is transferred from the atmosphere to seawater of the ria. Another is the opposite case, when upwelling eases off (July 7th) and there is an outflow (8 molC s^{-1}) to air.

The contribution of carbon due to freshwater

This is only important in times of strong river flow and is 2 molC s^{-1} during the rest of the year. Due to the granitic nature of Galician soil, the contribution of inorganic carbon to the freshwater is very small. The major discharge of organic carbon to the ria of Vigo comes from the sewer outlet of the town of Vigo, which in summer reaches 80% of the total due to freshwater.

The interchange of carbon with the sediment

This contributes carbon during the winter period, as indicated by 26 molC s^{-1} for February, as well as by a calculation for the 31st of January (10 molC s^{-1} based on PREGO et al. (1988) data for all the ria of Vigo as a box), which is not included in this work. The storms from the southeast, common in winter, resuspend the fine fraction of the sediment, which is then transported away from the ria (NOMBELA et al., 1987). During the rest of the year the bed of the ria receives an average of 27 molC s^{-1}.

Formation and redissolution of carbonate

Calcium carbonate dissolves principally in winter and forms in summer, above all during the time of strong circulation. The formation of calcium carbonate occurs in both layers in spring and summer due to its biological utilization. However, because net fluxes for four of the six sampling periods were within the margin of error for Table 7, it would be interesting to make a Ca^{2+} and Mg^{2+} balance in the ria.

The effect of four cited biogeochemical processes is the exchange of carbon with the surrounding coastal water. In winter, when the contributions of freshwater are high, the situation must be similar to that in February. A large quantity of carbon is exported to the ocean, 78 molC s^{-1}, which is derived almost equally from the above mentioned sources. During the rest of the year the opposite occurs; the ria behaves like a carbon trap, with most of the 27 molC s^{-1} that is trapped being lost to sedimentation.

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APPENDIX 1

CA0 and NO concepts

Recently, a compositional relation for 0:C:N:P of 175:129:17:l has been reported for the phytoplankton of the ria of Vigo (RIOS and FRAGA, 1987). From this ratio and the forms of nutrient salts and inorganic carbon in seawater, the following equation is derived

$$129HCO_3 + 17NO_3 + HPO^2{}_4 + 126H_2O$$
$$= (C_{129}H_{234}N_{17}0_{70}P) + 1750_2 + 1480H^- . \qquad (15)$$

When selecting a component of each part of the photosynthesis remineralisation equation, i.e., O_2 and HCO_3 and its stoichometric quotients, 175:129 (1.36), the resulting parameter, CA0 (or NO; BROECKER, 1974). is unaffected by photosynthesis and remineralization processes. According to PREGO (1988) and RIOS et al. (1989), they are

$$\text{“CAO”} = [0_2]$$
$$+ 1.36([C0_2] - C_{ar}) - 0.5[N0_2] – 2[NH^+{}_4] \qquad (16)$$

$$\text{“NO”} = [0_2] + 10{,}29[N0_3] + 9.79[N0_2] + 8{,}29[N\ NH^+{}_4], \qquad (17)$$

where $C_{ar} = 0.5(Alk + [N0_3] + 0.45[N0_2] - [N\ NH^+{}_4])$. The correction terms for nitrite and ammonia are a recognition that these two substances can reduce the calculated oxygen production during photosynthesis. The correction for “C_{ar}” reflects the consumption of carbonate for the formation of the skeleton of some marine organisms. This is proportional to the alkalinity (Alk).

FIG. 1. The southernmost ria of Galicia is that of Vigo, which has a length of 33 km, an area of 156 km^2, and a capacity of 3.3 km^2. The ria of Vigo can be partitioned into five boxes by a series of cross sections (S), whose characteristics are given in Table 1. The location of sampling stations numbered 1 to 9 is given in the upper left part of the figure.

FIG. 2. The general circulation in the ria of Vigo (PREGO and FRAGA, 1992) permits the division of the ria in five boxes (B1 to B5) with two layers (upper layers: L2 to L5, and lower layers: L20 to L50) and the establishment of the seawater fluxes represented by "F." External to each ria box is the flux "F_r" which represents the contribution of freshwater. Box 1 is shallow and is not divided into two layers.

FIG. 3. The interchanges of carbon established for a box in the ria of Vigo are due to photosynthesis (P), particle sinking (D), remineralisation (R), and sedimentation (S), as well as to precipitation or redissolution of carbonate in the upper layer "Cs" and lower layer "Cd" and the air-water transfer of CO_2 (C). All of these interchanges and processes are net values (result of opposite fluxes as indicated by the pairs of arrows), and they are positives if they are inputs to a layer and negatives if they are outputs.

FIG. 4. Mass balance (in molC s^{-1} for the ria as a whole) for organic carbon in the ria of Vigo. Different seasonal situations are illustrated by three cases. (a) February 28th, (b) May 26th, and (c) September 4th. Inputs of organic carbon [according to arrow direction or sign of photosynthesis (P) and remineralization (R)] to a layer are positives and output negatives.

FIG. 5. Map of isopleths of salinity (Practical Salinity Units), temperature, nitrate, and chlorophyll a for May 26th, 1986, from PREGO et al. (1988). The position of the stations is given in Fig. 1.

FIG. 6. Man of isopleths of salinity (Practical Salinity Units), temperature, nitrate, and chlorophyll a for September 4th. 1986, from PREGO et al. (1988):

FIG. 7. Variation of sinking of particulate organic carbon from the upper layer, remineralization, and sedimentation in the lower layer with respect to net

photosynthesis in the upper layer (Fig. 3) . Units are in molC s^{-1}. Data from Table 6: according to the sign criteria, negative values are inorganic carbon outputs of a layer (e.g., photosynthesis) and opposite (e.g., remineralization). On February 28th remineralization was higher than photosynthesis, and net photosynthesis has a positive value.

TABLE 1. Characteristics of the boxes into which the ria of Vigo was divided. The position is shown in Fig. 1.

TABLE 2. Fluxes ($1O^3$ kg s^{-1}) of “Q” (according to subsections and layers of Fig. 2) and “R” (without considering rain and evaporation on seawater) calculated for the ria of Vigo in accordance with a stationary box-model proposed by PREGO and FRAGA (1992) on the basis of the flow of freshwater and salinity as a tracer.

TABLE 3. Average concentration of “CAO” (in mol O_2 kg^{-1}), inorganic and organic carbon (C_{ing} and C_{org} in mol C kg^{-1}), and alkalinity (Alk in mol kg^{-1}) for the sections (upper subsections: M_s) to M_{59}; lower subsections: M_{s10} to M_{590}) and boxes (upper layer: M_{L2} to M_{L5}; lower layer: M_{L20} to M_{L50}) in the ria of Vigo (see Fig. 2). Concentrations in freshwater were calculated considering sewage, polluted, and unpolluted water, in accordance with FRAGA (1976), ALVAREZ (1980) PEREZ et al. (1987) and FREGO (1988).

TABLE 4. Ruxes of “CAO” (in mol O2 s^{-1}, inorganic and organic carbon (C_{ing} and C_{org} in mol C S^{-1}), and alkalinity (Alk in mol s^{-1}) in the ria of Vigo according to “F” in the box model shown in Figs. 1 and 2.

TABLE 5. Net fluxes due to biogeochemical processes for “CAO” (mol 0_2 s^{-1}), inorganic and organic carbon (C_{ing} and C_{org} in mol C S-1), and alkalinity (Alk in mol s^{-1}) in the ria of Vigo. This values were employed in solving System I, where AO, Al, A2, and A3 are “CAO” C_{ing}, C_{org} and Alk fluxes in the upper layer, and B1, B2, and B3 are C_{ing}, C_{org} and Alk fluxes in the lower layer of the ria.

TABLE 6. Results of solve System I. Units are in mol C s^{-1} “C” is CO_2 air-water interchanged; “Cs” and “Cd” are carbonate precipitation redissolution in upper and

lower layer; P, R, D, and S are net photosynthesis in upper layer, net remineralization in lower layer, sinking of particulate organic carbon (POC) from upper to lower layer, and net sedimentation of POC in lower layer. A positive sign is a layer or box input and a negative sign is an output. In box 1 there are not two layers since it is shallow and tides cause homogenization. There is the relation: 1 mol C s^{-1} = 1040/K mg C m^{-2} d^{-1}, where K is the surface of one or more boxes in km^2 (Table 1).

TABLE 7. Interchange of carbon between the ria of Vigo and its surroundings. A positive value indicates influx to the ria and a negative value an outflux from it. The values are in mol C s^{-1} ria^{-1}. “Fe” and “Fs” are the carbon fluxes (inorganic plus organic) entering and leaving, respectively, the ria.

TABLE 8. Oxygen, “Og” interchanged between the atmosphere and the seawater of the ria of Vigo. It has been calculated by “NO” balance from data of PREGO et al. (1988) as PREGO (1993) has indicated. Since “NO” is not involved in processes of photosynthesis remineralization, its balance in the upper layer is the oxygen air-water passage. Units are mol 0_2 s^{-1}. Inputs to ria are positive and outputs negative.

TABLE 9. Results, mol s^{-1}, of $[NO_3] + [NO_2] - [NH_4]$ balances (P3 + P2 - P4 in upper layers and R3 + R2 - R4 in lower layers) in the ria of Vigo. They have been calculated from fluxes of Table 2 and nitrate, nitrite, and ammonium data by PREGO et al. (1988). (P3 + P2 - P4) and (R3 + R2 - R4) in expressions (10) and (11) are corrections to alkalinity caused by the appearance or disappearance of strong ions in Eqn. 15.

Table 1

Box	km	km^2	km^3	Mean depth (m)
1	6.5	17.41	0.0434	2.5
2	6.3	10.13	0.1461	14.4
3	7.5	28.85	0.4888	16.9
4	6.9	59.65	1.4676	24.6
5	5.3	40.18	1.1292	28.1
Ria:	32.5	156.2	3.275	21.0

Table 2

	28 February	26 May	31 May	7 July	4 September	3 October
Q_{s1}	372	89	302	134	537	171
Q_{s2}	588	139	415	147	414	192
Q_{s3}	989	183	704	184	486	249
Q_{s4}	1049	280	675	249	711	211
Q_{s5}	1667	433	696	-	-	-
Q_{s9}	534	142	285	108	275	89
Q_{s10}	252	80	297	132	535	169
Q_{s20}	461	130	410	145	413	190
Q_{s30}	850	174	699	182	484	246
Q_{s40}	1012	303	916	294	875	247
Q_{s50}	1623	456	938	-	-	-
Q_{s90}	409	110	38	61	129	50
Q_{L2}	110	44	55	209	793	277
Q_{L3}	153	25	67	25	219	82
Q_{L4}	30	14	38	6	2	14
Q_{L5}	42	25	7	-	-	-
Q_{L20}	319	93	168	223	671	299

Q_{L30}	542	69	356	61	290	138
Q_{L40}	601	252	294	182	511	65
Q_{L50}	653	178	29	-	-	-
R1	118.1	8.4	5.4	1.9	1.3	2.5
R2	7.1	0.3	0.0	0.1	0.1	0.1
R3	9.0	0.7	0.3	0.4	0.4	0.5
R4	18.8	1.0	0.3	0.5	0.3	0.6
R5	5.0	0.2	0.0	0.1	0.0	0.1

Table 3

	28 February				26 May				31 May				7 July				4 September				3 October			
	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk
M_{S1}	1103	1329	64.9	1406	1327	1795	118.4	2017	1500	2072	79.1	2291	1381	1959	122.9	2231	1491	2061	78.3	2313	1478	2064	81.4	2238
M_{S2}	1286	1639	78.1	1757	1417	1923	100.5	2161	1512	2095	68.2	2310	I444	2024	101.4	2297	1544	2133	92.3	2334	1498	2127	71.9	2307
M_{S3}	1407	1855	63.4	2007	1445	1954	104.7	2209	1527	2106	71.2	2328	1454	2026	119.8	2310	1512	2093	87.8	2334	1508	2087	101.7	2319
M_{S4}	1463	1965	62.5	2144	1468	2010	83.2	2264	1527	2105	74.0	2331	1474	2050	86.8	2330	1505	2097	81.3	2347	1495	2094	73.9	2326
M_{S5}	1471	1998	61.5	2201	1475	2036	74.6	2288	1520	2090	71.4	2335	1477	2062	110.6	2333	1509	2111	73.3	2336	1481	2060	84.7	2330
M_{S9}	1404	1843	61.1	2003	1482	2038	63.6	2296	1509	2070	85.2	2328	1480	2061	101.2	2334	1520	2126	71.3	2331	1485	2060	96.8	2310
M_{S10}	1414	1894	70.0	2037	1456	2031	94.3	2227	1552	2137	74.2	2328	1418	1987	125.6	2269	1495	2082	75.7	2302	1480	2105	81.5	2263
M_{S20}	1494	2028	58.8	2206	1506	2112	70.1	2310	1527	2142	53.0	2323	1478	2136	113.0	2350	1511	2157	63.6	2333	1543	2210	68.7	2357

M_{S30}	1523	2093	27.9	2290	1516	2124	78.5	2324	1536	2157	53.4	2342	1491	2150	101.4	2353	1507	2156	59.1	2337	1530	2187	53.4	2346
M_{S40}	1522	2099	60.8	2308	1517	2124	70.6	2327	1537	2148	59.0	2340	1496	2146	78.0	2351	1513	2141	59.9	2328	1523	2185	51.6	2349
M_{S50}	1520	2100	60.2	2311	1516	2123	75.3	2329	1532	2137	57.2	2340	1522	2151	104.9	2348	1513	2156	57.7	2331	1535	2172	61.9	2348
M_{S90}	1522	2079	48.1	2279	1508	2091	63.8	2323	1529	2133	63.7	2335	1472	2116	105.1	2348	1515	2064	66.4	2336	1524	2165	78.0	2338
M_{L2}	1220	1530	74.5	1634	1383	1861	107.3	2106	1507	2086	72.6	2305	1419	1997	110.1	2271	1481	2170	89.9	2326	1499	2101	80.0	2280
M_{L3}	1354	1159	70.2	1895	1434	1943	101.0	2188	1520	2102	68.7	2321	1449	2026	109.8	2303	1539	2114	90.2	2332	1504	2109	90.8	2298
M_{L4}	1441	1918	62.6	2085	1464	1998	87.6	2253	1523	2098	76.3	2329	1469	2053	97.4	2329	1509	2099	86.1	2336	1497	2087	83.5	2320
M_{L5}	1463	1980	62.1	2171	1472	2025	79.0	2277	1524	2100	71.9	2334	1475	2063	99.8	2335	1507	2107	78.6	2337	1491	2078	79.2	2328
M_{L20}	1467	1984	65.5	2150	1493	2094	78.4	2286	1527	2145	62.2	2326	1450	2083	136.2	2321	1505	2148	66.6	2334	1522	2176	72.2	2324
M_{L30}	1511	2066	57.8	2255	1511	2117	77.1	2317	1534	2150	54.1	2332	1482	2141	111.4	2352	1506	2155	60.7	2335	1.540	2201	60.1	2353
M_{L40}	1524	2097	59.3	2301	1516	2124	71.5	2326	1537	2150	58.3	2340	1489	2151	93.0	2352	1512	2155	60.2	2337	1528	2184	54.3	2346

M_{L50}	1520	2092	59.9	2308	1516	2124	72.7	2328	1533	2139	59.2	2339	1496	2154	94.9	2350	1513	2153	58.7	2337	1532	2176	57.8	2347
M_{R1}	386	17	90	-50	331	13	130	-50	337	13	151	-50	323	12	241	-50	350	14	292	-50	336	13	210	-50
M_{R2}	386	17	88	-50	331	13	108	-50	337	13	111	-50	323	12	124	-50	350	14	117	-50	336	13	120	-50
M_{R3}	334	16	213	-50	-310	7	1718	-50	-1160	0	3860	-50	-789	3	2925	-50	-782	4	2925	-50	-526	5	2367	-50
M_{R4}	16	0	172	-50	-146	0	248	-50	-150	0	254	-50	-134	0	313	-50	-127	0	287	-50	-130	0	298	-50
M_{R5}	386	17	87	-50	331	13	106	-50	337	13	108	-50	323	12	121	-50	350	14	115	-50	336	13	118	-50

Table 4

	28 February				26 May				31 May				7 July				4 September				3 October			
	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk
F_{S1}	410.3	494.4	24.14	523.0	118.1	159.8	10.54	179.5	453.0	625.7	23.89	693.7	185.1	262.5	16.47	299.0	792.3	1106.8	42.05	1242.0	252.7	352.9	13.92	382.7

F_{S2}	756.2	963.7	45.92	1033.1	197.0	267.3	13.97	300.4	627.5	869.4	28.30	958.7	212.3	297.5	14.91	337.6	639.2	883.1	38.21	966.4	287.6	408.3	14.96	442.9
F_{S3}	1391.5	1834.6	62.70	1984.9	264.4	357.6	19.16	404.2	1075.0	1482.6	50.12	1638.9	267.5	372.8	22.04	425.0	734.8	1017.2	42.67	1134.3	375.5	519.7	25.32	577.4
F_{S4}	1534.7	2061.3	65.56	2249.1	411.0	562.8	23.30	633.9	1030.7	1420.9	49.95	1573.4	367.0	510.5	21.61	580.2	1070.1	1491.0	62.07	1667.0	315.4	441.8	15.59	490.8
F_{S5}	2452.2	3330.7	102.52	3669.1	638.7	881.6	32.30	990.7	1057.9	1454.6	49.69	1625.2												
F_{S9}	749.7	984.2	36.15	1069.6	210.4	289.4	9.03	326.0	430.1	590.0	24.28	663.5	159.8	222.6	10.93	252.1	418.0	584.7	19.61	642.7	132.2	183.4	8.62	205.6
F_{S10}	356.3	477.3	17.66	513.3	116.5	162.5	7.54	178.2	452.0	634.7	22.04	691.4	187.2	262.3	16.58	299.5	791.3	1113.9	40.50	1231.6	250.1	355.7	13.77	382.4
F_{S20}	688.7	934.9	27.12	1017.0	195.8	274,6	9.11	300.3	626.1	878.2	21.73	952.4	214.3	309.7	16.39	340.8	624.0	890.8	26.27	963.5	293.2	419.9	13.05	447.8
F_{S30}	1294.6	1779.1	49.22	1947.4	263.8	369.6	13.66	404.4	1073.7	1507.7	37.33	1637.1	271.4	391.3	18.45	428.2	729.4	1043.5	28.60	1130.9	376.4	538.0	13.14	577.1
F_{S40}	1540.3	2124.4	61.53	2335.7	459.7	643.6	21.39	705.1	1407.9	1967.6	54.04	2143.4	439.8	630.9	22.93	691.2	1323.9	1873.3	52.41	2045.8	377.7	539.7	12.75	580.2
F_{S50}	2467.0	3408.3	97.71	3750.8	691.3	968.1	34.34	1062.0	1437.0	2004.5	53.65	2194.9												
F_{S90}	622.5	850.3	19.67	932.1	165.9	230.0	7.02	255.5	58.1	81.1	2.42	88.7	89.8	129.1	6.41	143.2	195.4	266.2	8.57	301.3	75.2	108.3	3.90	116.9

$F_{L.2}$	134.2	168.3	8.20	179.7	60.9	81.9	4.72	92.7	82.9	114.7	3.99	126.8	296.6	417.4	23.01	474.6	1169.6	1641.5	71.29	1844.3	415.2	582.0	22.16	631.6
F_{L3}	207.2	269.1	10.74	289.9	35.9	48.6	2.53	54.7	101.8	140.8	4.60	155.5	36.2	50.7	2.75	57.6	337.0	463.0	19.75	510.7	123.3	172.9	7.45	188.4
F_{L4}	43.2	57.5	1.88	62.6	20.5	28.0	1.23	31.5	57.9	79.7	2.90	88.5	8.8	12.3	0.58	13.9	3.0	4.2	0.17	4.7	21.0	29.2	1.17	32.5
F_{L5}	61.4	83.2	2.61	91.2	36.8	50.6	1.98	56.9	10.7	14.7	0.50	16.3												
F_{L20}	468.0	632.9	20.90	685.9	138.8	194.7	7.29	212.6	256.6	360.4	10.45	390.8	323.4	464.5	30.37	517.6	1002.5	1441.2	44.69	1566.0	455.1	650.6	21.59	694.9
F_{L30}	819.0	1119.8	31.33	1222.2	104.3	146.9	5.32	159.9	546.1	765.4	19.26	830.2	90.4	130.6	6.80	143.5	436.7	625.0	17.60	677.2	212.5	303.7	8.29	324.7
F_{L40}	915.9	1260.3	35.64	1382.9	382.0	535.2	18.02	586.2	451.9	632.1	17.14	688.0	271.0	390.0	16.93	427.9	772.6	1101.2	30.76	1194.2	99.3	142.0	3.53	152.5
F_{L50}	992.6	1366.1	38.85	1507.1	269.8	378.1	12.94	414.4	44.5	62.0	1.72	67.8												
F_{R1}	45.69	2.0	10.63	-5.5	2.8	0.1	1.0	-0.4	1.8	0.1	0.82	-0.3	0.6	0.0	0.46	-0.1	0.5	0.0	0.38	-0.1	0.8	0.0	0.53	-0.1
F_{R2}	2.7	0.1	0.64	-0.3	0.1	0.0	0.03	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.01	0.0	0.0	0.0	0.01	0.0	0.0	0.0	0.01	0.0
F_{R3}	3.0	0.1	1.92	-0.4	-0.2	0.0	1.20	0.0	-0.3	0.0	1.16	0.0	-0.3	0.0	1.17	0.0	-0.3	0.0	1.17	0.0	-0.2	0.0	1.18	0.0

F_{R4}	0.3	0.0	3.23	-0.9	-0.1	0.0	0.25	-0.1	0.0	0.0	0.08	0.0	-0.1	0.0	0.16	0.0	0.0	0.0	0.09	0.0	-0.1	0.0	0.18	0.0
F_{R5}	1.9	0.1	0.44	-0.2	0.1	0.0	0.02	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.01	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.01	0.0

Table 5

		28 February				26 May				31 May			
Box	Layer	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk
1	-	+8.4	+15.1	-4.2	+15.2	-1.2	-2.8	+1.9	+1.7	-0.8	-9.1	+1.0	+2.6
2	L2	+9.4	+4.6	+8.4	+4.2	+0.9	-5.3	+0.8	+1.4	+0.8	-2.0	-2.1	+1.0
	L20	+1.4	+7.0	+3.3	+2.5	-1.4	+0.7	+1.0	-2.2	-0.4	+2.2	+6.8	+3.0
3	L3	+20.5	+20.1	-5.7	+19.9	-1.0	-8.0	+1.2	-1.4	+3.2	-11.4	+6.0	+5.5
	L30	+5.9	+6.5	-1.5	+1.9	+0.4	+3.3	-1.8	+1.1	-3.3	-4.9	-0.9	-10.0
4	L4	+19.9	+8.1	+2.0	+14.4	-4.5	-12.6	-3.9	+1.1	-8.2	-24.1	+9.8	-1.5
	L40	+4.5	+7.2	+1.8	-0.1	-0.3	+3.2	+2.0	1.5	+1.7	+11.4	-4.9	+4.3
5	L.5	-15.6	-13.6	+0.3	+4.3	-5.4	-8.7	-2.0	-0.7	-6.6	-13.6	+1.5	+0.3
	L50	+4.5	-1.0	+0.1	+0.8	+1.4	+3.0	-2.0	+0.6	+4.7	+10.4	-1.6	0.0
Ria	upper	+43	+34	+8	+58	+12	-37	-2	+2	12	-60	+13	+8

	lower	+16	+20	+4	+5	0	+9	-1	-2	+3	+19	+3	-3
Ria	-	+59	+54	+12	+63	+12	-28	-3	0	-9	-41	+16	+5

		7 July				4 September				3 October			
Box	Layer	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk	CA0	C_{ing}	C_{org}	Alk
1	-	-2.7	+0.2	-0.6	-0.4	+0.5	-7.1	+1.2	+10.5	+1.8	-2.8	-0.4	+0.4
2	L2	+0.4	-12.1	-8.9	-4.4	+6.4	-23.4	+22.7	+5.1	-5.0	-13.2	+1.6	-3.0
	L20	-0.3	-0.3	+7.6	+1.7	+7.8	+22.9	-12.4	-10.1	-3.2	+4.4	+0.2	-2.1
3	L3	+ 1.0	-4.6	+1.9	+1.5	-3.8	-27.9	+5.4	+1.4	-1.3	-19.4	+8.3	-1.8
	L30	-2.9	-1.7	+2.0	-1.5	-5.7	+9.5	-4.5	-0.9	+6.0	+12.7	+0.8	+7.9
4	L4	-2.9	-17.4	-6.0	-6.7	-16.3	-38.5	+8.3	-14.1	-6.2	-7.3	-3.7	-1.0
	L40	+4.0	+9.0	+5.5	+7.8	-20.3	+1.1	-1.8	-18.1	-0.8	+2.8	-1.2	0.0
5	L5												
	L50												
Ria	upper	-4	-34	-14	-10	-13	-97	+38	+3	-11	-43	+6	-5
	lower	+1	+7	+15	+8	-18	+34	-19	-29	+2	+20	+1	+5
Ria	-	-3	-27	+1	-2	-31	-63	+19	-26	-9	-23	+5	0

Table 6

	28 February							26 May							31 May						
Box	C	Cs	Cd	P	D	R	S	C	Cs	Cd	P	D	R	S	C	Cs	Cd	P	D	R	S
1	+5	+7	-	+3	-1	-	-1	0	+1	-	-4	-2	-	-2	+2	+1	-	-12	-11	-	-11
2	-8	+3	+2	+11	+19	+6	+27	0	+1	-1	-6	-5	+2	-3	+2	+1	+2	-4	-6	+1	+2
3	+7	+11	+1	+2	-4	+6	0	-2	-1	0	-6	-4	+3	-3	+6	+2	-5	-19	-13	0	-14
4	+11	+7	0	-10	-8	+7	+1	+2	0	0	-14	-18	+4	-12	-6	-2	+3	-17	-7	+9	-3
5	-16	+3	0	0	0	-1	-1	0	-1	0	-8	-10	+3	-9	-1	0	0	-12	-14	+10	-2
Ria	-1	+31	+3	+5	+6	+18	+26	0	0	-1	-38	-39	+12	-29	+3	0	0	-64	-51	+20	-28

	7 July							4 September							3 October						
Box	C	Cs	Cd	P	D	R	S	C	Cs	Cd	P	D	R	S	C	Cs	Cd	P	D	R	S
1	0	0	-	0	-1	-	-1	0	+5	-	-12	-11	-	-10	+1	0	-	-4	-4	-	-4
2	-3	-2	+1	-7	-15	-1	-9	+13	0	-4	-36	-14	+25	-3	-3	-2	-1	-9	-7	+5	-1
3	-2	+1	-1	-3	-2	-2	-1	+1	0	0	-28	-23	+9	-18	0	-1	+3	-19	-10	+9	-1
4	-3	-4	+4	-10	-16	+5	-6	-2	-9	-9	-28	-19	+11	-10	+2	0	0	-9	-12	+3	-11
Ria	-8	-5	+4	-20	-34	+2	-17	+12	-4	-13	-104	-67	+45	-41	0	-3	+2	-41	-33	+17	-17

Table 7

	28 February	26 May	31 May	7 July	4 September	3 October
Fe-Fs	-78	+27	+23	+24	+44	+16
CO_2	-1	0	+3	-8	+12	0
Freshwater	+19	+3	+2	+2	+2	+2
Sediment	+26	-29	-28	-17	-41	-17
$CaCO_3$	+34	-1	0	-1	-17	–1

Table 8

	28 February	26 May	31 May	7 July	4 September	3 October
B1	-2.3	-1.2	-3.8	-3.3	+1.1	+1.2
L2	+20.8	+0.7	-1.3	+4.9	-11.2	-1.0
L3	+10.7	+1.6	-4.4	+3.7	-4.4	-1.6
L4	+5.0	-7.1	-0.4	+1.7	-13.7	-8.8
L5	+5.8	-5.9	-4.7	no data	no data	no data
Ria	+40	-12	-15	+7	-28	-10

Table 9

	28 February	26 May	31 May	7 July	4 September	3 October
P2 + P3 – P4						
B1	+0.8	+0.2	+0.5	0.0	+0.2	+0.1
L2	-0.8	+0.1	+0.4	0.0	+4.4	0.0
L3	-3.0	0.0	+1.9	+0.1	+2.2	+0.3
L4	-0.1	+1.5	+2.0	+0.3	+3.5	+0.3
L5	-0.6	+1.0	+0.4	no data	no data	no data
Ria	-4	+3	+6	0	+10	+1
R3 + R2 – R4						
L20	-0.6	+0.1	0.0	0.0	-2.0	+0.2
L30	-0.2	+0.4	-0.2	+0.3	-1.1	+0.8

L40	+0.2	-0.1	-0.9	+0.1	+0.2	+0.1
L50	+0.3	0.0	-0.4	no data	no data	no data
Ria	0	0	-2	0	-3	+l